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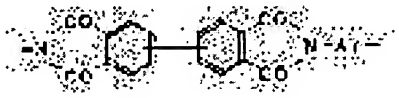
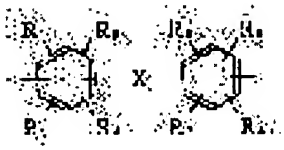
(71) Applicant : **UBE IND LTD**
(72) Inventor : **NAKANISHI SHUNSUKE**
ITO KENJI
KUSUKI YOSHIHIRO

(54) AROMATIC POLYIMIDE, SEMIPERMEABLE MEMBRANE, AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To obtain an arom. polyimide which is excellent in spinnability and film-forming properties and can easily form a high-strength asymmetric hollow yarn membrane excellent in gas permeability and selectivity by selecting a polyimide having specific repeating units.
CONSTITUTION: This arom. polyimide has repeating units represented by formula I {wherein Ar is an arom. diamine residue represented by formula II or III [wherein at least one of R1-R4 of formula II and R1 to R8 of formula III is SO3M (wherein M is an alkali metal) and the rest are H or a 1-3C alkyl; and X is a direct bond, O, SO2, NH, a 1-3C alkylene, alkyldine, or alkenylene]} and is obtd. by polymerizing and imidating about equimolar amts. of a biphenyltetracarboxylic acid compd. and an arom. diamine compd. represented by formula IV or V [wherein at least one of R1 to


I


II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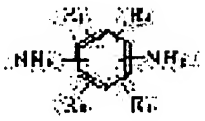
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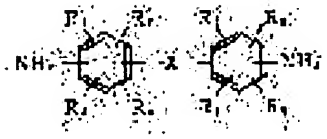
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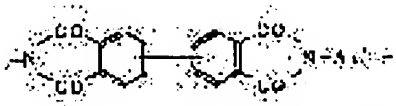
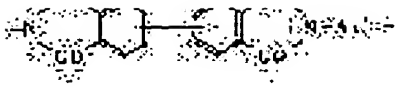

VI

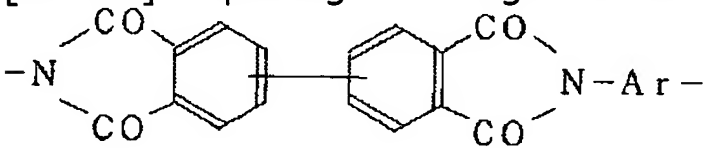


R4 of formula IV and R1 to R8 of formula V is SO3NL4 (wherein L is H or a 1-5C alkyl)] in a phenolic solvebt and treating the resulting arom. polyimide represented by the formula VI (wherein Ar' is a residue of a group of formula IV or V) with an alkali metal hydroxude or alkoxide.

* NOTICES *

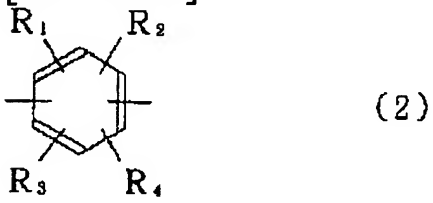
CLAIMS

[Claim(s)]
[Claim 1]A repeating unit is a general formula (1),[Formula 1]



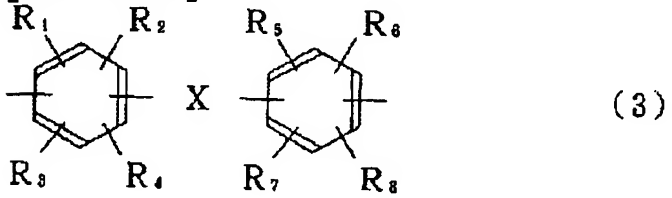
(1)

Aromatic polyimide come out of and expressed. However, Ar in a general formula (1) is the aromatic diamine residue shown in the following general formula (2) and (3), and at least one of R_1 in general formula (2) type - the R_4 is a $-SO_3M$ basis. As for [M, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and at least one of R_1 in a general formula (3) - the R_8 is a $-SO_3M$ basis. As for others, [M shows the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.
[Formula 2]



(2)

[Formula 3]



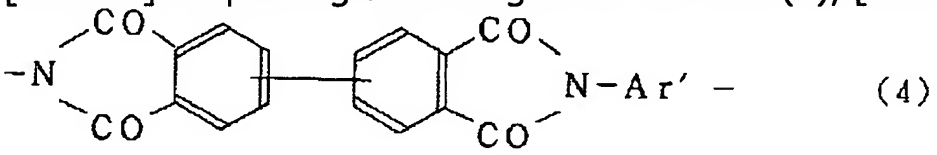
(3)

[Claim 2]aromatic diamine residue which Ar in a general formula (1) shows in the general formula (2) and (3) -- at least one of R_1 in general formula (2) type - the R_4 -- a $-SO_3M$ basis As for [M, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by

alkaline metal], and at least one of R_1 in a general formula (3) - the R_8 is a $-SO_3M$ basis. The aromatic polyimide according to claim 1, as for whose [M, others are an alkyl group of a hydrogen atom or the carbon numbers 1-3 in alkaline metal] and whose X is direct coupling.

[Claim 3]aromatic diamine residue which Ar in a general formula (1) shows in a general formula (2) -- at least one of R_1 in general formula (2) type - the R_4 -- a $-SO_3M$ basis The aromatic polyimide according to claim 1 whose others of [M are hydrogen atoms in alkaline metal].

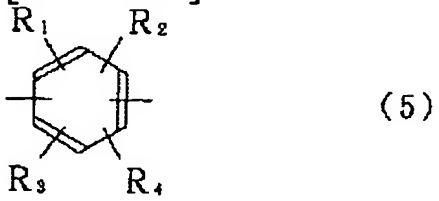
[Claim 4]A repeating unit is a general formula (4), [Formula 4]



(4)

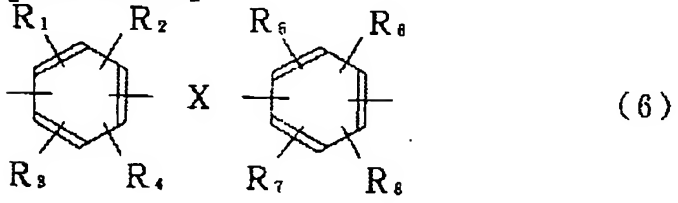
A process of the aromatic polyimide according to claim 1 coming out and processing the aromatic polyimide expressed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal. However, Ar' in a general formula (4) is the aromatic diamine residue shown in the following general formula (5) and (6), and at least one of R_1 in general formula (5) type - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (6) - the R_8 is a $-SO_3N(L)_4$ group. As for others, [L shows the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.

[Formula 5]



(5)

[Formula 6]



(6)

[Claim 5]Ar' in a general formula (4) is the aromatic diamine residue shown in the general formula (5) and (6), and at least one of R_1 in general formula (5) type - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (6) - the R_8 is a $-SO_3N(L)_4$ group. A process of the aromatic polyimide

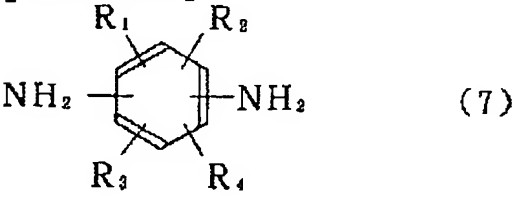
according to claim 4, as for whose [L, others are an alkyl group of a hydrogen atom or the carbon numbers 1-3 in alkyl group] of a hydrogen atom or the carbon numbers 1-5 and whose X is direct coupling.

[Claim 6]Ar' in a general formula (4) is the aromatic diamine residue shown in a general formula (5), and at least one of R_1 in general formula (5) type - the R_4 is a $-SO_3N(L)_4$ group.

A process of the aromatic polyimide according to claim 4 whose others of [L are hydrogen atoms in alkyl group] of a hydrogen atom or the carbon numbers 1-5.

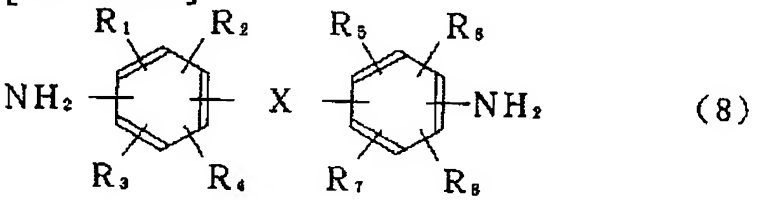
[Claim 7]General formula [a biphenyl tetracarboxylic acid compound and] (7) Reach (8).

[Formula 7]



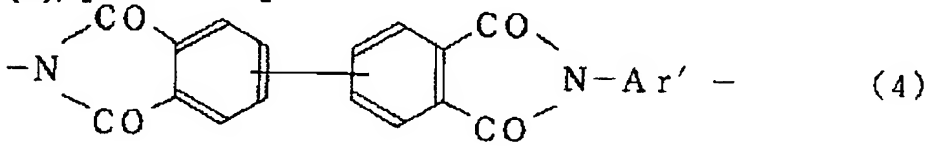
(7)

[Formula 8]



(8)

It is alike, abbreviation equimolar with the shown aromatic diamine compound is imide[a polymerization and]-ized in a phenol system solvent, and a repeating unit is a general formula (4), [Formula 9]



(4)

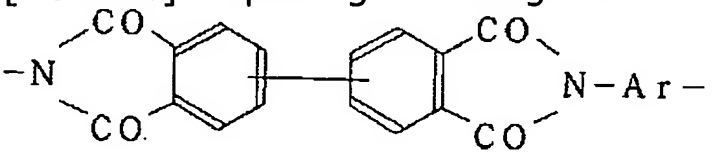
It comes out, the aromatic polyimide expressed is obtained, this polyimide is processed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal, and it is a $-SO_3M$ basis about the $-SO_3N(L)_4$ group of this polyimide. A process of the aromatic polyimide according to claim 4 changing [M into alkali-metal-ion]. However, at least one of R_1 in a general formula (7) - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (8) - the R_8 is a $-SO_3N(L)_4$ group. Others of [L are the alkyl groups of a hydrogen atom or the carbon numbers 1-3 in alkyl group] of a hydrogen atom or the carbon numbers 1-5, X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group, and Ar' in a general formula (4) shows the aromatic diamine residue shown in the above-mentioned general formula (7) and (8).

[Claim 8]An aromatic diamine compound is an aromatic diamine compound shown in the

general formula (7) and (8), and at least one of R_1 in general formula (7) type - the R_4 is a - $SO_3N(L)_4$ group. As for [L, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (8) - the R_8 is a $-SO_3N(L)_4$ group. Others of [L are the alkyl groups of a hydrogen atom or the carbon numbers 1-3 in alkyl group] of a hydrogen atom or the carbon numbers 1-5, A process of the aromatic polyimide according to claim 7 which X is direct coupling and is the diamine residue of an aromatic diamine compound which Ar' in a general formula (4) shows in the above-mentioned general formula (7) and (8).

[Claim 9]An aromatic diamine compound is an aromatic diamine compound shown in a general formula (7), and at least one of R_1 in a general formula (7) - the R_4 is a $-SO_4N(L)_4$ group. A process of the aromatic polyimide according to claim 7 which is the diamine residue of an aromatic diamine compound which, as for [L, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of the carbon numbers 1-5, and Ar' in a general formula (4) shows in the above-mentioned general formula (7).

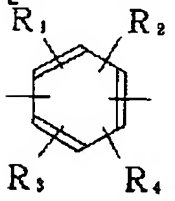
[Claim 10]A repeating unit is a general formula (1), [Formula 10]



(1)

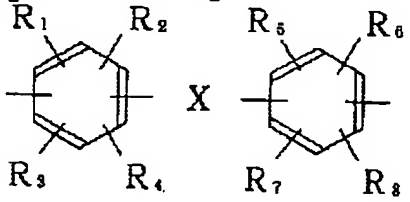
The aromatic polyimide semipermeable membrane with which it is come out and expressed. However, Ar in a general formula (1) is the aromatic diamine residue shown in the following general formula (2) and (3), and at least one of R_1 in general formula (2) type - the R_4 is a - SO_3M basis. As for [M, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and at least one of R_1 in a general formula (3) - the R_8 is a - SO_3M basis. As for others, [M shows the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.

[Formula 11]



(2)

[Formula 12]

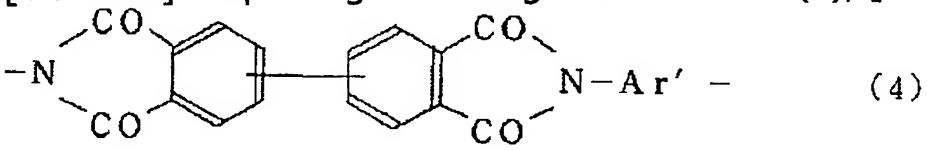


(3)

[Claim 11]aromatic diamine residue which Ar in a general formula (1) shows in the general formula (2) and (3) -- at least one of R_1 in general formula (2) type - the R_4 -- a $-SO_3M$ basisAs for [M, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and at least one of R_1 in a general formula (3) - the R_8 is a $-SO_3M$ basis. The aromatic polyimide semipermeable membrane according to claim 10, as for whose [M, others are an alkyl group of a hydrogen atom or the carbon numbers 1-3 in alkaline metal] and whose X is direct coupling.

[Claim 12]aromatic diamine residue which Ar in a general formula (1) shows in a general formula (2) -- at least one of R_1 in general formula (2) type - the R_4 -- a $-SO_3M$ basis The aromatic polyimide semipermeable membrane according to claim 10 whose others of [M are hydrogen atoms in alkaline metal].

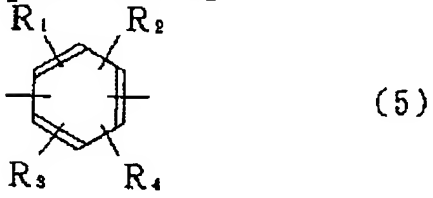
[Claim 13]A repeating unit is a general formula (4), [Formula 13]



(4)

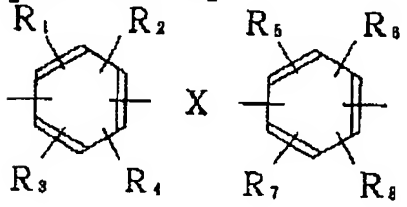
A process of the aromatic polyimide semipermeable membrane according to claim 10 coming out and processing an aromatic polyimide semipermeable membrane with which it is expressed by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal. However, Ar' in a general formula (4) is the aromatic diamine residue shown in the following general formula (5) and (6), and at least one of R_1 in general formula (5) type - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (6) - the R_8 is a $-SO_3N(L)_4$ group. As for others, [L shows an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and X shows direct coupling, -O-, $-SO_2-$, -NH-, an alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.

[Formula 14]



(5)

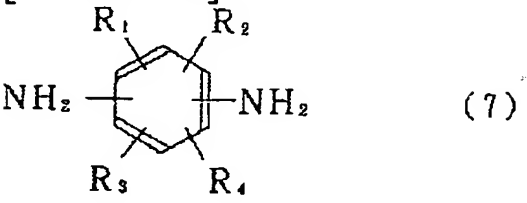
[Formula 15]



(6)

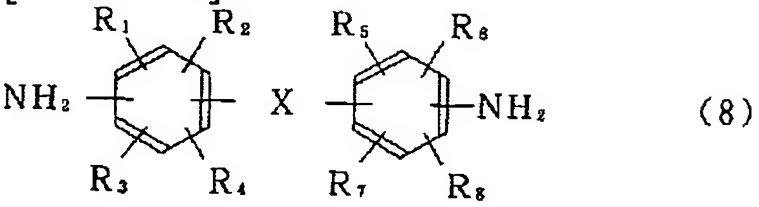
[Claim 14]General formula [a biphenyl tetracarboxylic acid compound and] (7) Reach (8).

[Formula 16]



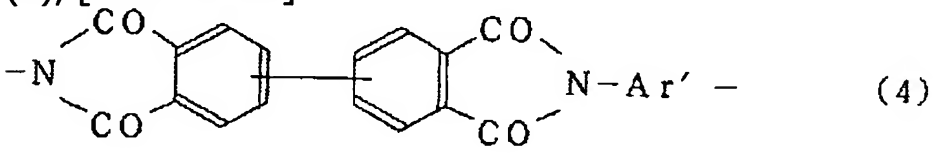
(7)

[Formula 17]



(8)

It is alike, abbreviation equimolar with the shown aromatic diamine compound is imide[a polymerization and]-ized in a phenol system solvent, and a repeating unit is a general formula (4), [Formula 18]



(4)

It comes out, the aromatic polyimide semipermeable membrane with which it is expressed is obtained, this polyimide semipermeable membrane is processed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal, and it is a $-SO_3M$ basis about the $-SO_3N(L)_4$ group of this polyimide semipermeable membrane. A process of the aromatic polyimide semipermeable membrane according to claim 13 changing [M into alkaline metal]. However, at least one of R_1 in a general formula (7) - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (8) - the R_8 is a $-SO_3N(L)_4$ group. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group, and Ar' in a general formula (4) shows the aromatic diamine residue shown in the above-mentioned general formula (7) and (8).

[Claim 15]An aromatic diamine compound is an aromatic diamine compound shown in the general formula (7) and (8), and at least one of R_1 in general formula (7) type - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show an alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (8) - the R_8 is a $-SO_3N(L)_4$ group. Others of [L are the alkyl groups of a hydrogen atom or the carbon numbers 1-3 in alkyl group] of a hydrogen atom or the carbon numbers 1-5, A process of the aromatic polyimide semipermeable membrane according to claim 14 which X is direct coupling and is the diamine residue of an aromatic diamine

compound which Ar' in a general formula (4) shows in the above-mentioned general formula (7) and (8).

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to aromatic polyimide, a semipermeable membrane, and its process. This invention relates to the process of aromatic polyimide and the aromatic polyimide semipermeable membrane which have a sulfonic acid alkali-metal-salt group in a polyimide skeleton, and aromatic polyimide, and the process of an aromatic polyimide semipermeable membrane in detail.
[0002]
[Description of the Prior Art]Aromatic polyimide is industrially used so much, for example as a film, a sheet, mold goods, a hollow filament, a varnish, etc. as the electronic industry material field, the electric insulation field, the gas separation field, a medical field, etc. Generally aromatic polyimide carries out the polycondensation of the abbreviation equimolar of aromatic tetracarboxylic dianhydride like a pyromellitic anhydride, and aromatic diamine like diaminodiphenyl ether in an organic solvent, and is used as polyamide acid, Subsequently, it is manufactured by heating or imide-izing polyamide acid in an acid anhydride like an acetic anhydride.
[0003]These days, the polyimide which has a sulfonic group, a sulfonic acid alkali salt group, sulfonic acid ammonium, etc. in a polyimide skeleton is proposed. For example, the aromatic diamine which does not have aromatic diamine, sulfonic acid ammonium, etc. which have aromatic tetracarboxylic acid, sulfonic acid ammonium, etc. in JP,6-87957,A, A polycondensation is carried out in an organic solvent like N-methyl pyrrolidone, it is made polyamide acid, and the copoly imide manufactured by 2 step-polymerization method subsequently imide-ized in triethylamine and an acid anhydride (formation of chemicals imide) and its process are indicated. Only the copoly imide which uses as a copolymerization ingredient aromatic diamine residue which has sulfonic acid ammonium is indicated in the gazette, and anything does not have an indication about gay polyimide. There is no indication also about a 1 step-polymerization method. Although there is a statement which includes tetracarboxylic acid very wide range as a general formula of aromatic tetracarboxylic acid, there is no concrete statement about biphenyl tetracarboxylic dianhydride.
[0004]The aromatic polyimide gas permeation membrane which serves as aromatic tetracarboxylic acid from the copoly imide which uses as a copolymerization ingredient the

screw phenylfluorenediamine which has a sulfonic group as diamine is indicated by JP,5-192552,A. The homogeneous membrane which used N-methyl pyrrolidone for the example of the gazette as a solvent, and uses for it benzophenone tetracarboxylic acid and the screw phenylfluorenediamine which has a sulfonic group as diamine as a copolymerization ingredient is indicated. To JP,63-283704,A and JP,63-283707,A. Homogeneous membranes which serve as pyromellitic dianhydride from the copoly imide which uses as a copolymerization ingredient the diaminobenzene sulfonic acid which has a sulfonic acid alkali-metal-salt group as diamine as aromatic tetracarboxylic acid, such as permselective membrane and a polyampholyte demarcation membrane, are indicated. The ion-exchange membrane of the polyimide which becomes JP,58-153541,A from the diamine which has aliphatic acid dianhydride, a sulfonic group, or a sulfonic acid alkali salt group is indicated.

[0005]If a sulfonic group, a sulfonic acid alkali-metal-salt group, sulfonic acid ammonium, etc. which are high polarity are introduced into a polyimide skeleton, the permeability of gas, selectivity, etc. will improve. using it for an asymmetric hollow fiber, carrying out, in order to use polyimide as an efficient gas separation membrane practical -- the maximum thing -- it is desirable. However, even if the polyimide which has these bases by which the indication proposal is made conventionally did not have spinning nature and enough film production nature, and-izing could not be carried out [hollow fiber], or the art of hollow-fiber-izing is not established or it could carry out [hollow fiber]-izing, there was a difficulty that a membranous mechanical strength is inferior.

[0006]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide aromatic polyimide and an aromatic polyimide semipermeable membrane excellent in the spinning nature which is excellent in the permeability of gas, and selectivity, and can form the asymmetric hollow fiber of high intensity easily, and film production nature. The spinning nature which this invention excels [nature] in the permeability of gas, and selectivity, and can form the asymmetric hollow fiber of high intensity easily, It aims at providing the principal chain skeleton excellent in film production nature with the process of aromatic polyimide and the process of an aromatic polyimide semipermeable membrane which have a sulfonic acid alkali-metal-salt group.

[0007]This invention persons inquired [aromatic polyimide / which has a sulfonic group, a sulfonic acid alkali-metal-salt group, sulfonic acid ammonium, etc.] wholeheartedly about aromatic tetracarboxylic dianhydride of a raw material, aromatic diamine, manufacturing conditions, etc. especially. As a result, ** biphenyl tetracarboxylic acid compound, for example, biphenyl tetracarboxylic dianhydride, and the aromatic diamine which has a sulfonic group and a sulfonic acid alkali-metal-salt group, . [whether in a phenol system solvent or an amide system solvent, a polymerization and imide-izing are impossible, and] Or aromatic polyimide of biphenyl tetracarboxylic acid and the aromatic diamine which has a sulfonic group and a sulfonic acid alkali-metal-salt group, Since it is insoluble to the inside of a phenol system solvent, or an amide system solvent, a semipermeable membrane like a hollow fiber cannot be obtained by the conventional method, ** A biphenyl tetracarboxylic acid compound, for example, biphenyl tetracarboxylic dianhydride, If the aromatic diamine which has sulfonic acid ammonium is made to react in a phenol system solvent, A polymerization and the aromatic

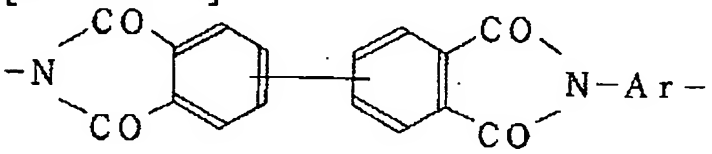
polyimide which is imide-ized and has sulfonic acid ammonium are obtained in one step, The aromatic polyimide which has a sulfonic acid alkali-metal-salt group in a principal chain skeleton easily when the aromatic polyimide which has this sulfonic acid ammonium is processed by hydroxide of an alkaline metal or the alkoxide of an alkaline metal is obtained, ** The aromatic polyimide semipermeable membrane from which sulfonic acid ammonium was changed into the sulfonic acid alkali-metal-salt group when the aromatic polyimide which has sulfonic acid ammonium was used as the semipermeable membrane and processed by hydroxide of an alkaline metal or the alkoxide of the alkaline metal is obtained, ** According to the polymerization and the method of making it imide-ize for the aromatic diamine which has biphenyl tetracarboxylic dianhydride and sulfonic acid ammonium in a phenol system solvent, the knowledge of the ability to attain said purpose was carried out, and it resulted in this invention.

[0008]

[Means for Solving the Problem]

[0009]As for this invention, a repeating unit is a general formula (1), [0010]

[Formula 19]



(1)

[0011]It comes out and is related with the aromatic polyimide expressed. However, Ar in a general formula (1) is the aromatic diamine residue shown in the following general formula (2) and (3), and at least one of R_1 in general formula (2) type - the R_4 is a $-SO_3M$ basis. As for

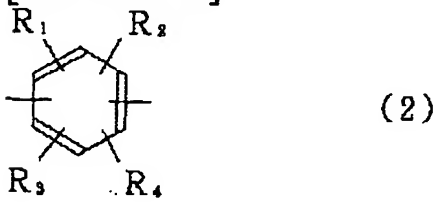
[M, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and at least one of R_1 in a general formula (3) - the R_8 is a $-SO_3M$ basis. As for others,

[M shows the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3,

an alkylidene group, or an alkenylene group.

[0012]

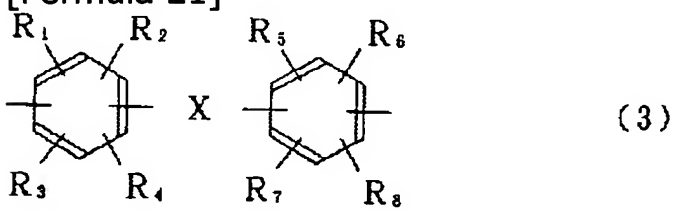
[Formula 20]



(2)

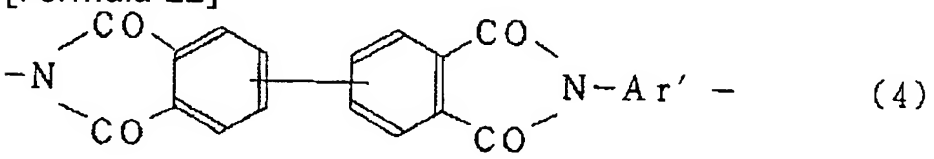
[0013]

[Formula 21]



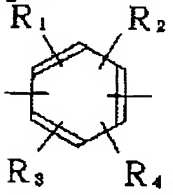
(3)

[0014]As for this invention, a repeating unit is a general formula (4), [0015]
[Formula 22]



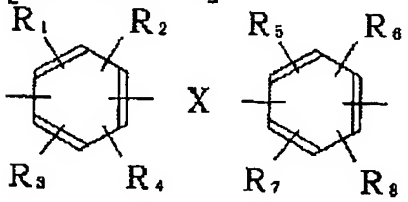
(4)

[0016]It is related with the process of aromatic polyimide expressed with the general formula (1) coming out and processing the aromatic polyimide expressed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal.
[0017]However, Ar' in a general formula (4) is the aromatic diamine residue shown in the following general formula (5) and (6), and at least one of R_1 in general formula (5) type - the R_4 is a $-SO_3N(L)_4$ group. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (6) - the R_8 is a $-SO_3N(L)_4$ group. As for others, [L shows the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.
[0018]
[Formula 23]



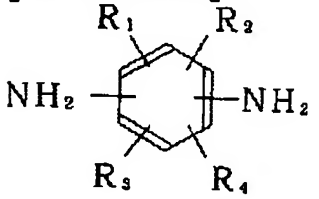
(5)

[0019]
[Formula 24]



(6)

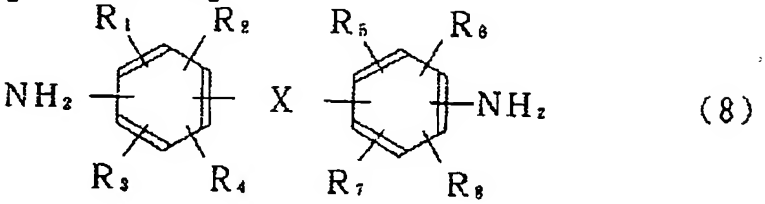
[0020]General formula [a biphenyl tetracarboxylic acid compound and] (7) This invention reaches (8).
[0021]
[Formula 25]



(7)

[0022]

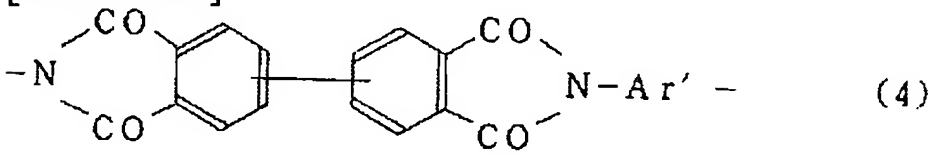
[Formula 26]



(8)

[0023]It is alike, abbreviation equimolar with the shown aromatic diamine compound is imide [a polymerization and]-ized in a phenol system solvent, and a repeating unit is a general formula (4), [0024]

[Formula 27]



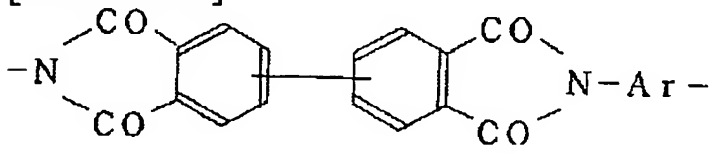
(4)

[0025]It comes out, the aromatic polyimide expressed is obtained, this polyimide is processed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal, and it is a $-SO_3M$ basis about the $-SO_3N(L)_4$ group of this polyimide. [M is related with the process of the aromatic polyimide according to claim 1 changing into alkaline metal].

[0026]However, at least one of R_1 in a general formula (7) - the R_4 is $-SO_3N(L)_4$. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (8) - the R_8 is $-SO_3N(L)_4$. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, X shows direct coupling, -O-, $-SO_2-$, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group, and Ar' in a general formula (4) shows the diamine residue of the aromatic diamine compound shown in the above-mentioned general formula (7) and (8).

[0027]As for this invention, a repeating unit is a general formula (1), [0028]

[Formula 28]



(1)

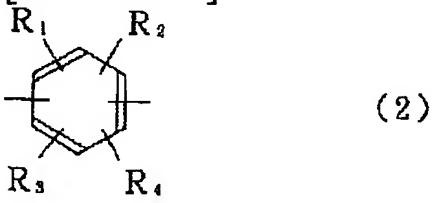
[0029]It comes out and is related with the aromatic polyimide semipermeable membrane with which it is expressed.

[0030]However, Ar in a general formula (1) is the aromatic diamine residue shown in said general formula (2) and (3), and at least one of R_1 in general formula (2) type - the R_4 is a $-SO_3M$ basis. As for [M, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkaline metal], and at least one of R_1 in a general formula (3) - the R_8 is a $-SO_3M$ basis. As for others, [M shows the alkyl group of a hydrogen atom or the carbon

numbers 1-3 by alkaline metal], and X shows direct coupling, -O-, -SO_2-, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.

[0031]

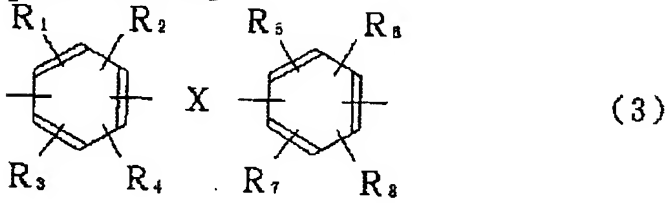
[Formula 29]



(2)

[0032]

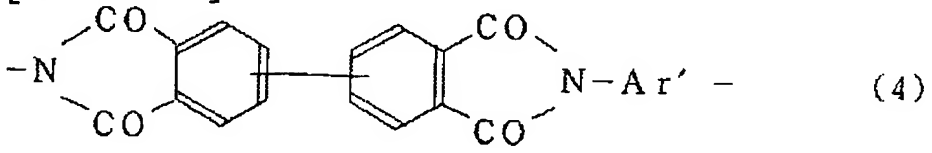
[Formula 30]



(3)

[0033]As for this invention, a repeating unit is a general formula (4), [0034]

[Formula 31]



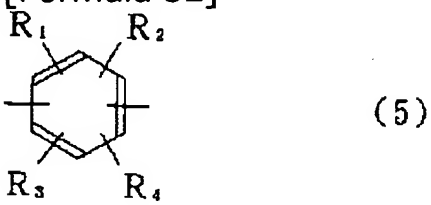
(4)

[0035]It is related with the process of an aromatic polyimide semipermeable membrane expressed with the general formula (1) coming out and processing the aromatic polyimide semipermeable membrane with which it is expressed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal.

[0036]However, Ar' in a general formula (4) is the aromatic diamine residue shown in the following general formula (5) and (6), and at least one of R_1 in general formula (5) type - the R_4 is a -$SO_3N(L)_4$ group. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (6) - the R_8 is a -$SO_3N(L)_4$ group. As for others, [L shows the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and X shows direct coupling, -O-, -SO_2-, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group.

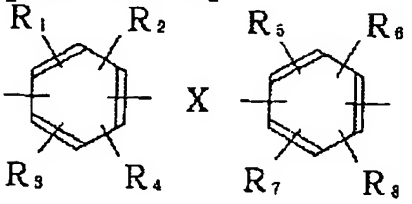
[0037]

[Formula 32]



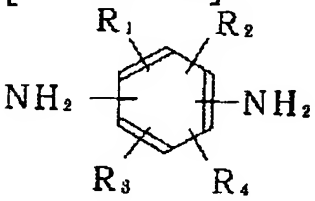
(5)

[0038]
[Formula 33]



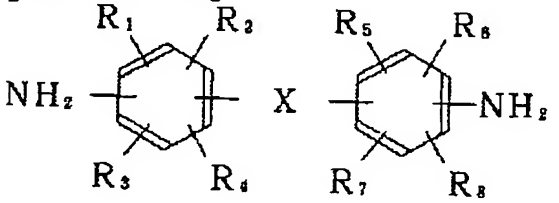
(6)

[0039]General formula [a biphenyl tetracarboxylic acid compound and] (7) This invention reaches (8).
[0040]
[Formula 34]



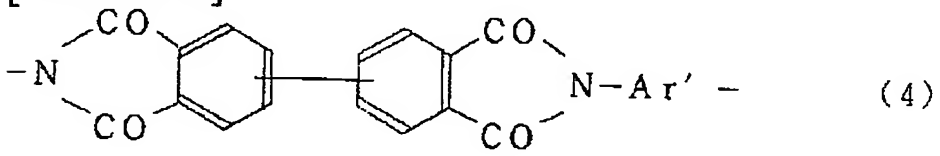
(7)

[0041]
[Formula 35]



(8)

[0042]It is alike, abbreviation equimolar with the shown aromatic diamine compound is imide [a polymerization and]-ized in a phenol system solvent, and a repeating unit is a general formula (4), [0043]
[Formula 36]



(4)

[0044]It comes out, the aromatic polyimide semipermeable membrane with which it is expressed is obtained, this polyimide semipermeable membrane is processed by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal, and it is a $-SO_3M$ basis about the $-SO_3N(L)_4$ group of this polyimide semipermeable membrane. [M is related with the process of an aromatic polyimide semipermeable membrane expressed with the general formula (1) changing into alkaline metal].
[0045]However, at least one of R_1 in a general formula (7) - the R_4 is $-SO_3N(L)_4$. As for [L, others show the alkyl group of a hydrogen atom or the carbon numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, and at least one of R_1 in a general formula (8) - the R_8 is $-SO_3N(L)_4$. As for [L, others show the alkyl group of a hydrogen atom or the carbon

numbers 1-3 by alkyl group] of a hydrogen atom or the carbon numbers 1-5, X shows direct coupling, -O-, -SO_2-, -NH-, the alkylene group of the carbon numbers 1-3, an alkylidene group, or an alkenylene group, and Ar' in a general formula (4) shows the aromatic diamine residue shown in the above-mentioned general formula (7) and (8).

[0046]In this invention, aromatic polyimide expressed with a general formula (1), If abbreviation equimolar of a biphenyl tetracarboxylic acid compound and an aromatic diamine compound which has sulfonic acid ammonium shown in said general formula (7) and (8) is imide[a polymerization and]-ized in a phenol system solvent, Aromatic polyimide which has sulfonic acid ammonium is obtained, and it is obtained by processing this by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal. However, when it replaces with a biphenyl tetracarboxylic acid compound and benzophenone tetracarboxylic acid and pyromellitic dianhydride are used, Even if it uses aromatic diamine for which it has sulfonic acid ammonium, in a phenol system solvent, it cannot polymerize and imide-ize in one step, or it is difficult a polymerization and for spinning nature and film production nature to be insufficient, and to obtain an asymmetric hollow fiber of high intensity, even if it can imide-ize. Even if it uses a biphenyl tetracarboxylic acid compound, it replaces with an aromatic diamine compound which has sulfonic acid ammonium, Also when diamine which has a sulfonic group (-SO_3H) and a sulfonic acid alkali-metal-salt group is used, in a phenol system solvent, cannot polymerize and imide-ize in one step, or Since it is insoluble to a phenol system solvent, Spinning nature and film production nature are insufficient, and it is difficult to obtain an asymmetric hollow fiber of high intensity.

[0047]In this invention, as a biphenyl tetracarboxylic acid compound, - biphenyl tetracarboxylic dianhydride, and 3, 3, 4, and 4 '2, 3, 3 and 4'-biphenyl tetracarboxylic dianhydride etc. can be mentioned, and these biphenyl tetracarboxylic acid, its ester, etc. can be used.

[0048]As an aromatic diamine compound which has sulfonic acid ammonium shown in the general formula (7) and (8), 2, 5-diaminobenzene sulfonic acid ammonium, 2, 5-diaminobenzene sulfonic acid trimethylammonium, 2, 5-diaminobenzene sulfonic acid triethyl ammonium, 2, 5-diaminobenzene sulfonic acid tributyl ammonium, 2 and 5-diaminobenzene sulfonic acid -- doria -- mill ammonium, 2, and 4-diaminobenzene sulfonic acid ammonium. 2, 4-diaminobenzene sulfonic acid trimethylammonium, 2, 4-diaminobenzene sulfonic acid triethyl ammonium, 2, 4-diaminobenzene sulfonic acid tributyl ammonium, 2, and 4-diaminobenzene sulfonic acid -- doria -- mill ammonium. 2, the 4-diaminobenzene 1, 5-disulfon acid ammonium, 2, the 4-diaminobenzene 1, 5-disulfon acid trimethylammonium, 2, the 4-diaminobenzene 1, 5-disulfon acid triethyl ammonium, 2, the 4-diaminobenzene 1, 5-disulfon acid tributyl ammonium, 2, the 4-diaminobenzene 1, and 5-disulfon acid -- doria -- mill ammonium. 3, 3 '- dimethyl 4 and 4'-diaminodiphenyl 5-sulfonic acid ammonium, 3, 3 '- dimethyl 4 and 4'-diaminodiphenyl 5-sulfonic acid trimethylammonium, 3, 3 '- dimethyl 4 and 4'-diaminodiphenyl 5-sulfonic acid triethyl ammonium, 3, 3 '- dimethyl 4 and 4'-diaminodiphenyl 5-sulfonic acid tributyl ammonium, 3 and 3 '- dimethyl 4 and 4'-diaminodiphenyl 5-sulfonic acid -- doria -- mill ammonium. The 3 and 3'-dimethyl 4, 4 '-diaminodiphenyl 6 and 6'-disulfon acid ammonium, The 3 and 3'-dimethyl 4, 4 '-

diaminodiphenyl 6 and 6'-disulfon acid trimethylammonium, The 3 and 3'-dimethyl 4, 4 '- diaminodiphenyl 6 and 6'-disulfon acid triethyl ammonium, 3 and 3 -- the - dimethyl 4, 4 '- diaminodiphenyl 6 and 6'-disulfon acid tributyl ammonium, and '3, 3' -- the - dimethyl 4 and 4 '- diaminodiphenyl 6 and 6'-disulfon acid -- doria -- mill ammonium and the benzidines 2 and 2 - disulfon acid ammonium. Benzidine 2, and 2 '- disulfon acid trimethylammonium and benzidine 2 and 2'-disulfon acid triethyl ammonium, benzidine 2, and 2 '- disulfon acid tributyl ammonium and benzidine 2 and 2'-disulfon acid -- doria -- mill ammonium. 4 and 4'-diamino diphenyl ether 2-sulfonic acid ammonium, 4 and 4'-diamino diphenyl ether 2-sulfonic acid trimethylammonium, 4 and 4'-diamino diphenyl ether 2-sulfonic acid triethyl ammonium, 4 and 4'-diamino diphenyl ether 2-sulfonic acid tributyl ammonium, 4 and 4'-diamino diphenyl ether 2-sulfonic acid -- doria -- mill ammonium. 4 and 4'-diamino diphenyl ether 3-sulfonic acid ammonium, 4 and 4'-diamino diphenyl ether 3-sulfonic acid trimethylammonium, 4 and 4' - diamino diphenyl ether 3-sulfonic acid tributyl ammonium, and - diamino diphenyl ether 3-sulfonic acid triethyl ammonium, 4, and 4 '4, 4'-diamino diphenyl ether 3-sulfonic acid -- doria -- mill ammonium. 4, 4 '- diamino diphenyl ether 2 and 2'-disulfon acid ammonium, 4, 4 '- diamino diphenyl ether 2 and 2'-disulfon acid trimethylammonium, 4, 4 '- diamino diphenyl ether 2 and 2'-disulfon acid triethyl ammonium, 4, 4 '- diamino diphenyl ether 2 and 2'-disulfon acid tributyl ammonium, 4 and 4 '- diamino diphenyl ether 2 and 2'-disulfon acid -- doria -- mill ammonium. 4 and 4'-diaminodiphenyl sulfone 3-sulfonic acid ammonium, 4 and 4'-diaminodiphenyl sulfone 3-sulfonic acid trimethylammonium, 4 and 4'-diaminodiphenyl sulfone 3-sulfonic acid triethyl ammonium, 4 and 4'-diaminodiphenyl sulfone 3-sulfonic acid tributyl ammonium, 4 and 4'-diaminodiphenyl sulfone 3-sulfonic acid -- doria -- mill ammonium, and 4 and 4 -- 'the - diaminodiphenyl sulfones 3 and 3' - disulfon acid ammonium, 4, and 4 '- diaminodiphenyl sulfone 3 and 3'-disulfon acid trimethylammonium. 4, 4 '- diaminodiphenyl sulfone 3 and 3'-disulfon acid triethyl ammonium, 4, 4 '- diaminodiphenyl sulfone 3 and 3'-disulfon acid tributyl ammonium, 4 and 4 '- diaminodiphenyl sulfone 3 and 3'-disulfon acid -- doria -- mill ammonium. 4, 4 '- diaminodiphenylmethane 2 and 2'-disulfon acid ammonium, 4, 4 '- diaminodiphenylmethane 2 and 2'-disulfon acid trimethylammonium, 4, 4 '- diaminodiphenylmethane 2 and 2'-disulfon acid triethyl ammonium, 4, 4 '- diaminodiphenylmethane 2 and 2'-disulfon acid tributyl ammonium, 4 and 4 '- diaminodiphenylmethane 2 and 2'-disulfon acid -- doria -- mill ammonium. 4, 4 '- diaminodiphenylmethane 3 and 3'-disulfon acid ammonium, 4, 4 '- diaminodiphenylmethane 3 and 3'-disulfon acid trimethylammonium, 4, 4 '- diaminodiphenylmethane 3 and 3'-disulfon acid triethyl ammonium, 4, 4 '- diaminodiphenylmethane 3 and 3'-disulfon acid tributyl ammonium, 4 and 4 '- diaminodiphenylmethane 3 and 3'-disulfon acid -- doria -- mill ammonium. 4 and 4'-diaminodiphenylamine 2-sulfonic acid ammonium, 4 and 4'-diaminodiphenylamine 2-sulfonic acid trimethylammonium, 4 and 4'-diaminodiphenylamine 2-sulfonic acid triethyl ammonium, 4 and 4'-diaminodiphenylamine 2-sulfonic acid tributyl ammonium, 4 and 4'-diaminodiphenylamine 2-sulfonic acid -- doria -- mill AMMONIU 4 and 4 '- diaminostilbene 2 and 2'-disulfon acid ammonium. 4, 4 '- diaminostilbene 2 and 2'-disulfon acid trimethylammonium, 4, 4 '- diaminostilbene 2 and 2'-disulfon acid triethyl ammonium, 4 and 4 -- 'the - diaminostilbene 2 and 2' - disulfon acid tributyl ammonium, 4, and 4 '- diaminostilbene 2 and 2'-disulfon acid -- doria -- mill ammonium etc. can be mentioned.

[0049]In this invention, as a phenol system solvent, the melting point of below about 100 degreeC is below 80 degreeC preferably, and since a problem of polymerization solution handling of a solvent in a polymerization solution being preferably frozen [the boiling point in ordinary pressure] by the following [280 degreeC] below as for 300 degreeC does not arise, it is suitable. Specifically, univalent phenols, such as phenol, o-, m- or p-cresol, 3,5-xylenol, carvacrol, and Timor, catechols, or halogenated phenols that replaced hydrogen of a benzene nucleus of univalent phenol with a halogen atom are preferred. A mixture may be sufficient as these solvents. As halogenated phenols, for example 3-KURORU phenol, 4-KURORU phenol, 3-bromine phenol, 4-bromine phenol, 2-4-bromine phenol, 2-clo roux 4-hydroxytoluene, 2-clo roux 5-hydroxytoluene, 3-clo roux 6-hydroxytoluene, 4-clo roux 2-hydroxytoluene, 2-bromine 4-hydroxytoluene, 2-bromine 5-hydroxytoluene, 3-bromine 6-hydroxytoluene, 4-bromine 2-hydroxytoluene, etc. can be mentioned, and especially 4-KURORU phenol is preferred also in halogenated phenols.

[0050]In this invention, a polymerization and imide-ization in a phenol system solvent, Abbreviation equimolar of a biphenyl tetracarboxylic acid compound and an aromatic diamine compound which has sulfonic acid ammonium is ordinarily dissolved in a phenol system solvent, Since rate of polymerization with practically sufficient carrying out by making it react, heating to reaction temperature of 130-200 degreeC preferably, and removing 100-250degreeC and water to generate is obtained and evaporation desorption of a solvent from a polymerization system can be suppressed, it is suitable. A reaction may be performed by a batch type or continuous system may perform.

[0051]A polycondensation reaction and an imide-ized reaction advance at reaction temperature, and a solution of polyimide which has the sulfonic acid ammonium dissolved in a phenol system solvent in one step is obtained. Reaction time is about 10 to 60 hours. The amount of aromatic diamine compound used which has a biphenyl tetracarboxylic acid compound and sulfonic acid ammonium to a phenol system solvent in that case, When quantity (concentration) of polyimide in a solvent uses especially polymerization liquid for manufacture of semipermeable membranes, such as a hollow fiber, directly five to 50% of the weight, concentration 10 to 40 % of the weight, It is preferred to make it become further 12 to 25% of the weight, and it is preferred that 10-8000 poise of rotation viscosity (it measures by 100 degreeC) of polymerization liquid is 100-3000 poise especially. Rotation viscosity is too too high, or if too low, a difficulty will arise to spinning nature and film production nature.

[0052]In this invention, aromatic polyimide which has a sulfonic acid alkali-metal-salt group, Heating, evaporation, etc. remove a phenol system solvent from a polyimide solution which has sulfonic acid ammonium, and it is obtained by subsequently processing by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal. Sulfonic acid ammonium is changed into a sulfonic acid alkali-metal-salt group by this processing. A semipermeable membrane from a solution of polyimide which has the sulfonic acid ammonium obtained by a polymerization and imide-ization. It can manufacture by obtaining a semipermeable membrane of polyimide which has sulfonic acid ammonium by the film production methods, such as a dry method, wet process, and a dryness-and-moisture type method, and processing this by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal. In mind a solution of polyimide which has especially sulfonic acid ammonium from flow casting or a making machine Regurgitation or

after extruding, Since the dryness-and-moisture type method which leads into a solidified solution, makes it solidify, and carries out the after-washing drying process of the adhesion solidified solution can obtain a semipermeable membrane which has a sulfonic acid alkali-metal-salt group with good permeability and selectivity by processing by hydroxide of an alkaline metal of a post process, or an alkoxide of an alkaline metal, it is preferred.
[0053]As a solidified solution used for wet process and a dryness-and-moisture type method at the time of obtaining a semipermeable membrane of polyimide which has sulfonic acid ammonium, For example, alcoholic solvent, such as water, methanol, ethanol, propanol, and isopropanol, A solvent of a polyimide solution and a polar solvent which has compatibility are used by mixed solvents, such as ketone solvent, such as acetone, methyl ethyl ketone, a diethyl ketone, and ethyl propyl ketone, these water, alcoholic solvent, and ketone solvent, etc. not dissolving polyimide. A mixed solvent with water, especially a mixed solvent of water and alcoholic solvent, for example, a mixed solvent of water and ethanol, can make an asymmetric semipermeable membrane excellent in permeability and selectivity without a defect form, and it is especially preferred.
[0054]A semipermeable membrane of polyimide which has the solidified sulfonic acid ammonium, Alcoholic solvent, such as methanol, ethanol, propanol, and isopropanol, washes this, Furthermore, an inert solvent, for example, isopentane, n-hexane, isooctane, Even if it processes by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal after heat-treating further, washing and desiccation with aliphatic hydrocarbon system solvents, such as n-heptane, and, It may process by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal by a damp or wet condition, without drying and heat-treating, or an unwashed thing may be processed.
[0055]In this invention, processing by hydroxide of an alkaline metal of a semipermeable membrane of polyimide or an alkoxide of an alkaline metal which has sulfonic acid ammonium is performed by contacting a semipermeable membrane in hydroxide of an alkaline metal, or an alkoxide content solution of an alkaline metal. Although a contact method in particular is not restricted, a method of carrying out dipping treatment of the semipermeable membrane to hydroxide of an alkaline metal or an alkoxide content solution of an alkaline metal is adopted suitably. 1 minute - 10 hours are preferably preferred for dipping treatment time for changing sulfonic acid ammonium into a sulfonic group for 1 second - 100 hours. As hydroxide of an alkaline metal, sodium hydroxide, a potassium hydrate, lithium hydroxide, cesium hydroxide, etc. are used. moreover -- as the alkoxide of an alkaline metal -- ARUKISHIDO of alkaline metals, such as sodium, potassium, lithium, and caesium, -- an alkoxide of the carbon numbers 1-5 is used preferably. Although hydroxide of an alkaline metal or an alkoxide content solution of an alkaline metal is ordinarily used as a solution of organic solvents, such as water, alcoholic solvent, a hydrocarbon system, ketone solvent, or a solution of these mixed solvents, 0.001-50 mol/l. I. is preferred for especially the concentration in 0.01-10 mol /. As for immersion temperature, near a room temperature is convenient, and preferred for it.
[0056]A semipermeable membrane which has the sulfonic acid alkali-metal-salt group produced by carrying out dipping treatment, After alcoholic solvent, such as methanol, ethanol, propanol, and isopropanol, washes and aliphatic hydrocarbon system solvents, such as an inert solvent, for example, isopentane, n-hexane, isooctane, and n-heptane, wash

further, it will heat-treat, if it is desiccation and also necessity. Since carrying out at a temperature lower than softening temperature or a second order transition point of a semipermeable membrane which has a sulfonic acid alkali-metal-salt group does not destroy asymmetric structure of an asymmetric semipermeable membrane, heat treatment temperature is preferred. It is carried out at temperature ordinarily chosen from temperature of 90-400 degreeC suitably.

[0057]In this invention, hollow fibers which can take a large effective membrane area as a demarcation membrane although it may be which shape, such as a film, a sheet shaped flat film, and a hollow filament-like hollow fiber, are preferred for shape of a semipermeable membrane of having a sulfonic acid alkali-metal-salt group. As a manufacturing method of a hollow fiber, a method indicated by JP,61-35282,B, JP,1-44804,B (USP.4460526), JP,6-93988, B, etc., for example can be referred to. Next, although one example of a manufacturing method with a preferred hollow fiber is explained in this invention, this invention is not limited to this example.

[0058]A solution of polyimide which has the sulfonic acid ammonium imide[a polymerization and]-ized in a phenol system solvent is used as dope liquid, After extruding in mind from a nozzle for hollow filament spinning and making a hollow filament-like molded product form, After making it a polyimide hollow fiber which leads a molded product into a solidified solution, solidifies it, washes with alcoholic solvent and an aliphatic hydrocarbon system solvent, and has sulfonic acid ammonium, If it processes by hydroxide of an alkaline metal, or an alkoxide of an alkaline metal, a hollow fiber which has an asymmetric sulfonic acid alkali-metal-salt group suitable as a demarcation membrane will be obtained.

[0059]A solution of polyimide which, more particularly, has the sulfonic acid ammonium imide [a polymerization and]-ized in a phenol system solvent is used as dope liquid, Nozzle discharge temperature for spinning 60from nozzle for hollow filament spinning -150degreeC, Rotation viscosity in 70-120 degreeC preferably 10-10000 poise, After extruding 100-6000-poise dope liquid in mind and making a hollow filament-like molded product form especially, A molded product in the minus 10 - plus 60degreeC, and a holding [to minus 5- plus 40 degreeC]-preferably solidified solution, Lead into alcoholic solvent or a mixed solvent of water and alcoholic solvent as a solidified solution preferably, and it is made to solidify, alcoholic solvent -- and -- or, after making it a polyimide hollow fiber which washes with an aliphatic hydrocarbon system solvent and has sulfonic acid ammonium, Concentration of 0.001-50 mol/l. of hydroxide of an alkaline metal or an alkoxide of an alkaline metal is preferably immersed in a 0.01-10 mol/l. solvent solution for 1 second - 10 hours for 1 second - 100 hours, Although sulfonic acid ammonium of polyimide is changed into a sulfonic acid alkali-metal-salt group, It is necessary to change into a sulfonic acid alkali-metal-salt group no sulfonic acid ammonium of polyimide which constitutes a hollow fiber. Concentration and immersion time of hydroxide of an alkaline metal or a solution of an alkoxide of an alkaline metal may be adjusted, and only sulfonic acid ammonium of polyimide which constitutes an outside surface of a hollow fiber which are a part of hollow fiber, especially a gaseous preferential segregation layer may be changed into a sulfonic acid alkali-metal-salt group. alcoholic solvent after changing sulfonic acid ammonium of polyimide into a sulfonic acid alkali-metal-salt group -- and -- or, if an aliphatic hydrocarbon system solvent washes, a washing solvent is evaporated at temperature

of 50-150 degreeC and it dries, If dry stress relief heat treatment is furthermore carried out, a hollow fiber which has an asymmetric sulfonic acid alkali-metal-salt group suitable as a demarcation membrane will be obtained.

[0060]Thus, an obtained hollow fiber is high intensity, and selectivity and permeability are extremely excellent and can use it conveniently as a demarcation membrane. It is suitable for separation of separation of mixed gas, for example, separation of oxygen-nitrogen, separation of helium nitrogen, hydrogen separation, carbon dioxide separation, etc. especially as a gas separation membrane.

[0061]

[Effect of the Invention]According to this invention, it excels in spinning nature and film production nature, and the aromatic polyimide semipermeable membrane which has aromatic polyimide and the sulfonic acid alkali-metal-salt group which have a sulfonic acid alkali-metal-salt group with high permeability of gas and selectivity can be provided. The polymerization of the aromatic polyimide which has sulfonic acid ammonium excellent in spinning nature and film production nature according to this invention, By being able to perform imide-ization in one step and processing this by hydroxide of an alkaline metal, or the alkoxide of an alkaline metal, The asymmetric hollow fiber which has a sulfonic acid alkali-metal-salt group of the high intensity which could obtain the aromatic polyimide which has a sulfonic acid alkali-metal-salt group easily, and was excellent in the permeability of gas and selectivity can be manufactured easily.

[0062]

[Example]In each example, a hollow fiber, the pipe made from a stainless steel, and epoxy resin adhesive were used for the permeation performance of a hollow fiber, it created the bundles hollow fiber for permeation performance evaluation, and stored and modularized this in the container made from a stainless steel. The effective membrane area of the bundles hollow fiber was about 5-cm^2. The gas which introduced the mixed gas of helium/O_2/ N_2=30/30 / 40 (volume ratio) into module, and the differential pressure of the outside of a hollow fiber and the inside introduced into it by 10 kg/cm^2 was contacted to the outer surface of the hollow fiber, and was made to penetrate inside a hollow fiber. The transmission rate (P') of each gas was computed from the measured value of gas chromatography analysis of penetration gas and unpenetrated gas. Measurement temperature was 50degreeC. The unit of a transmission rate (P') is Ncc/(cm^2, sec., and cmHg).

[0063]Examples 13, 3, and 4 and 4'-biphenyl tetracarboxylic dianhydride (BPDA) 99 millimol, 2,4-diaminobenzene sulfonic acid triethyl ammonium (mDABS-Et_3N) 100 millimol with 4-KURORU phenol 195g. It puts into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached, The polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring for 45 hours, and the solution of the aromatic polyimide which has sulfonic acid triethylammonium of 23 % of the weight of concentration dissolved in 4-KURORU phenol was prepared.

[0064]The solution of the aromatic polyimide which has sulfonic acid triethylammonium filtered this at the wire gauze made from a stainless steel of 400 meshes, and prepared the dope liquid for spinning. The dope liquid for spinning is a nozzle for hollow filament spinning

(the outer diameter of a circular opening part: 1000 micrometers) about this. Slit width of a circular opening part : It teaches the spinning device provided with 200 micrometers and outer diameter:400micrometer of a core part opening, After making it breathe out in the shape of a hollow filament in the air and passing the inside of a dry nitrogen gas atmosphere for a hollow filament-like molded product subsequently from the nozzle for hollow filament spinning, It is immersed in a primary solidified solution with a temperature [C] of 0 degree which consists of 80% of the weight of an ethanol solution, Made between guidance rolls go back and forth in secondary consolidation liquid with a temperature [in the secondary consolidation device provided with the guidance roll of a couple / C] of 0 degree, the coagulation of the hollow filament-like molded product was made to complete, and it was considered as the humid film in the air, and spinning was carried out while the taking over roll took over by taking over speed 15 m/min.

[0065]The hollow filament humid film of the aromatic polyimide which has the obtained sulfonic acid triethylammonium, After rolling this round in the bobbin and fully washing by ethanol, it was immersed in the ethanol solution of 1 mol/l. of sodium METOKI side for 3 seconds under the room temperature, and sulfonic acid triethylammonium was changed into the sulfone sodium group. After fully washing by ethanol after immersion and replacing ethanol by isooctane subsequently, the asymmetric aromatic polyimide hollow fiber which heats to 100 degreeC, performs evaporation and desiccation of isooctane, heat-treats for 30 minutes at the temperature of 270 more degreeC, and has a sulfone sodium group was obtained. The outer diameter of the hollow fiber was 350 micrometers, and thickness was 60 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0066]The asymmetric aromatic polyimide hollow fiber which time to immerse the aromatic polyimide humid film of example 2 Example 1 in the ethanol solution of a sodium METOKI side was replaced with from 3 seconds at 10 seconds, and also has a sulfone sodium group like Example 1 was obtained. The outer diameter of the hollow fiber was 350 micrometers, and thickness was 57 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0067]The asymmetric aromatic polyimide hollow fiber which time to immerse the aromatic polyimide humid film of example 3 Example 1 in the ethanol solution of a sodium METOKI side was replaced with from 3 seconds at 30 seconds, and also has a sulfone sodium group like Example 1 was obtained. The outer diameter of the hollow fiber was 345 micrometers, and thickness was 60 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0068]The ethanol solution of 1 mol/l. of sodium METOKI side of example 4 Example 1, The asymmetric aromatic polyimide hollow fiber which replaced with 0.05 mol/l. of sodium hydroxide solution, and time to immerse an aromatic polyimide humid film further was replaced with from 3 seconds at 30 seconds, and also has a sulfone sodium group like Example 1 was obtained. The outer diameter of the hollow fiber was 349 micrometers, and thickness was 62 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0069]The ethanol solution of 1 mol/l. of sodium METOKI side of example 5 Example 1, The

asymmetric aromatic polyimide hollow fiber which replaced with 0.05 mol/l. of sodium hydroxide solution, and time to immerse an aromatic polyimide humid film further was replaced with from 3 seconds in 1 minute, and also has a sulfone sodium group like Example 1 was obtained. The outer diameter of the hollow fiber was 353 micrometers, and thickness was 60 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0070]The ethanol solution of 1 mol/l. of sodium METOKI side of example 6 Example 1, The asymmetric aromatic polyimide hollow fiber which replaced with 0.05 mol/l. of sodium hydroxide solution, and time to immerse an aromatic polyimide humid film further was replaced with from 3 seconds in 3 minutes, and also has a sulfone sodium group like Example 1 was obtained. The outer diameter of the hollow fiber was 350 micrometers, and thickness was 62 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0071]The primary solidified solution in the case of the spinning of the solution of the aromatic polyimide which has sulfonic acid triethylammonium of example 7 Example 1 (80% of the weight of ethanol solution) is replaced with 60% of the weight of an ethanol solution, The asymmetric aromatic polyimide hollow fiber which time to immerse an aromatic polyimide humid film furthermore was replaced with from 3 seconds at 30 seconds, and also has a sulfone sodium group like Example 1 was obtained. The outer diameter of the hollow fiber was 349 micrometers, and thickness was 61 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0072]Examples 83, 3, and 4 and 4'-biphenyl tetracarboxylic dianhydride (BPDA) 99 millimol, 3,3'-dimethyl 4,4'-diaminobiphenyl 5-sulfonic acid triethyl ammonium (OST-Et_3N) 100 millimol with 4-KURORU phenol 341g. It puts into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached, The polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring for 45 hours, and the solution of the aromatic polyimide which has sulfonic acid triethylammonium of 16 % of the weight of concentration dissolved in 4-KURORU phenol was prepared.

[0073]The solution of the aromatic polyimide which has sulfonic acid triethylammonium filtered this at the wire gauze made from a stainless steel of 400 meshes, and prepared the dope liquid for spinning. The dope liquid for spinning is a nozzle for hollow filament spinning (the outer diameter of a circular opening part: 1000 micrometers) about this. Slit width of a circular opening part : It teaches the spinning device provided with 200 micrometers and outer diameter:400micrometer of a core part opening, After making it breathe out in the shape of a hollow filament in the air and passing the inside of a dry nitrogen gas atmosphere for a hollow filament-like molded product subsequently from the nozzle for hollow filament spinning, It is immersed in a primary solidified solution with a temperature [C] of 0 degree which consists of 80% of the weight of an ethanol solution, Made between guidance rolls go back and forth in secondary consolidation liquid with a temperature [in the secondary consolidation device provided with the guidance roll of a couple / C] of 0 degree, the coagulation of the hollow filament-like molded product was made to complete, and it was considered as the humid film in the air, and spinning was carried out while the taking over roll took over by taking over speed 15 m/min.

[0074]After the hollow filament humid film of the aromatic polyimide which has the obtained sulfonic acid triethylammonium rolled this round in the bobbin, fully washed it by ethanol and replaced ethanol by isooctane, it was heated to 100 degreeC and performed evaporation and desiccation of isooctane. This dry hollow fiber was immersed in the ethanol solution of 1 mol/l. of sodium METOKI side for 10 seconds under the room temperature, and sulfonic acid triethylammonium was changed into the sulfone sodium group. After fully washing by ethanol after immersion and replacing ethanol by isooctane subsequently, the asymmetric aromatic polyimide hollow fiber which heats to 100 degreeC, performs evaporation and desiccation of isooctane, heat-treats for 30 minutes at the temperature of 270 more degreeC, and has a sulfone sodium group was obtained. The outer diameter of the hollow fiber was 358 micrometers, and thickness was 65 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0075]The asymmetric aromatic polyimide hollow fiber which time to immerse an aromatic polyimide humid film in the ethanol solution of 1 mol/l. of sodium METOKI side of example 9 Example 8 was replaced with from 10 seconds at 30 seconds, and also has a sulfone sodium group like Example 8 was obtained. The outer diameter of the hollow fiber was 362 micrometers, and thickness was 65 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0076]The asymmetric aromatic polyimide hollow fiber which time to immerse an aromatic polyimide humid film in the ethanol solution of 1 mol/l. of sodium METOKI side of example 10 Example 8 was replaced with from 10 seconds in 1 minute, and also has a sulfone sodium group like Example 8 was obtained. The outer diameter of the hollow fiber was 360 micrometers, and thickness was 61 micrometers. The permeation performance evaluation result of this asymmetric aromatic polyimide hollow fiber is shown in Table 1.

[0077]

[Table 1]

表1

実施例	透過速度（注）		選択性（分離度）	
	P' He	P' O_2	P' He／P' N_2	P' O_2／P' N_2
実施例1	2．0	0．06	109	3．4
実施例2	1．5	0．05	157	5．3
実施例3	1．6	0．05	144	4．6
実施例4	7．9	0．29	111	4．1
実施例5	7．6	0．27	156	5．6
実施例6	7．7	0．22	168	4．9
実施例7	8．0	0．23	68	2．0
実施例8	4．8	0．39	32	2．6
実施例9	5．7	0．46	26	2．1
実施例10	5．4	0．43	28	2．2

(注)：(10^{-5}Ncc／(cm^2・sec・cmHg)

[0078]The comparative examples 13, 3, and 4 and 4'-biphenyl tetracarboxylic dianhydride (BPDA) 99 millimol, 2,4-diaminobenzene sulfone sodium (mDABS-Na) 100 millimol with 4-KURORU phenol 227g. Although it put into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached and the polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring for 4 hours, polymer deposited and the solution of homogeneous aromatic polyimide was not obtained.
[0079]The comparative examples 23, 3, and 4 and 4'-biphenyl tetracarboxylic dianhydride

(BPDA) 99 millimol, 2 and 4-diaminobenzene sulfone sodium (mDABS-Na) 100 millimol with 227 g of N-methyl pyrrolidone. Although it put into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached and the polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring for 35 hours, the polymerization solution was gelled and hollow-fiber-izing was difficult.

[0080]The comparative examples 33, 3, and 4, 4'-biphenyl tetracarboxylic dianhydride (BPDA) 99 millimol, and 2 and 4-diaminobenzene sulfonic acid (mDABS) 100 millimol with 4-KURORU phenol 217g. Although it put into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached and the polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring for 5 hours, polymer deposited and the solution of homogeneous aromatic polyimide was not obtained.

[0081]Comparative example 4 pyromellitic dianhydride (PMDA) 99 millimol and 2 and 4-diaminobenzene sulfonic acid triethyl ammonium (mDABS-Et_3N) 100 millimol, Although it put into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached and the polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring with 4-KURORU phenol 227g for 10 hours, polymer became muddy and the solution of homogeneous aromatic polyimide was not obtained.

[0082]The comparative examples 53, 3, and 4 and 4'-biphenyl tetracarboxylic dianhydride (BPDA) 99 millimol, 2 and 4-diaminobenzene sulfonic acid triethyl ammonium (mDABS-Et_3N) 100 millimol with 218 g of N-methyl pyrrolidone. Although it put into the separable flask in which the agitator and the nitrogen gas introducing pipe were attached and the polymerization and the imide-ized reaction were performed at the temperature of 160 degreeC under stirring for 40 hours, the polymerization solution gelled and hollow-fiber-izing was difficult.

[Translation done.]